THINK





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UST Branch Announces New Analytical Requirements for TAME and TBA

by Pat Ellis

On January 18, 2000, the EPA Office of Underground Storage Tanks issued a memorandum urging states to "begin monitoring and reporting of MTBE and other oxygenates in groundwater at all UST release sites nationwide." The Delaware UST Branch began requiring analysis for MTBE at the time of tank removal and during subsequent investigations when it made the transition to DERBCAP — Delaware's risk-based corrective action program, in early 1999. Since the introduction of DERBCAP, a number of companies have, at the request of the UST Branch, been analyzing for two of the other common gasoline oxygenates.

Data from these analyses show that there has been considerable use of the oxygenates tertiary amyl methyl ether (TAME), and tert-butyl alcohol (TBA) within the state. The UST Branch is therefore adding the requirement to analyze for both TAME and TBA at any sites where MTBE is required as an analyte. This includes facilities where gasoline, kerosene, jet fuels, used oil, or aviation gas has been stored (see DERBCAP Guidance Document, Table 2). The announcement of the additional analytical requirements was first made at the UST Branch's recent conference, Tanks 2001 - A Tank Odyssey. For existing LUST sites, project officers will be notifying RPs and their consultants of the new requirement. Although not adding other oxygenates at the current time, such as ETBE, DIPE, or ethanol, the UST Branch strongly encourages at least a one-time analysis for other oxygenates to determine their presence or absence at a site.

Analytical methods

A recently published article by Halden and others (2001) reviewed the standard methods for the analysis of MTBE and other oxygenates in gasoline-contaminated groundwater. Consistently good results were obtained with EPA Method 8240B/60B (mass spectrometry) and ASTM method D4815 (flame ionization detection). EPA Method 8020A/21B (photoionization detection) was unfit for monitoring of TBA and frequently yielded false-positive and inaccurate results when ether oxygenates were monitored in aqueous samples containing high concentrations of TPH (>1000 μ g/L).

Characteristics of TAME

TAME can be added to gasoline to meet the oxygenate requirements of the Clean Air Act, or it can be added to gasoline to increase the octane content. Based on some of the LUST sites where TAME has been studied in Delaware, the dissolved TAME levels can be as high as the MTBE levels in groundwater. The solubility of pure TAME in water is approximately 20,000 ppm. Experimental and theoretical solubility of TAME from a reformulated gasoline mixture (with TAME being used to meet all of

the 2% by weight oxygen requirement) is in the 1200-1300 ppm range. The taste threshold for TAME is somewhat higher than that of MTBE (128 µg/L versus 20-40 µg/L), but its odor threshold is lower (27 ppb versus 53 ppb). Unfortunately, little information is available on the toxicity of TAME, so the Department will develop DERBCAP RBSLs (riskbased screening levels) based on the aesthetic properties. TAME falls between benzene and MTBE in its ability to sorb to soils and be retarded in its movement in the subsurface, so plume lengths should be shorter than MTBE plumes. Likewise, TAME is somewhat easier than MTBE to remove from groundwater using carbon filters but is nearly as difficult as MTBE to remove from water by air stripping.

Characteristics of TBA

TBA can be present in gasoline for a number of reasons: (1) TBA can be added to gasoline to meet part of the oxygenate requirement for reformulated gasoline; (2) TBA occurs as an impurity due to an incomplete reaction during the manufacture of MTBE; and (3) TBA also occurs as an intermediate in the biodegradation of MTBE. Whatever the reason for its presence, it can also occur at significant dissolved levels in groundwater. TBA is completely

soluble in water, so even small amounts originally present in gasoline can result in high levels in groundwater. As indicated by its organic carbon partition coefficient (K_{oc}), TBA is somewhat more retarded in its movement through soils than MTBE, but after TBA reaches groundwater, it is even more difficult to remove by carbon filters or air stripping. From a toxicological point of view, TBA



shows evidence of carcinogenicity. The California Department of Health Services

has established a Drinking Water Action Level of 12 μ g/L for TBA (CDHS establishes health-based advisory levels for chemicals for which primary MCLs have not been adopted.) The odor threshold for TBA is 21 ppm, so it can be present in drinking water and not be detected by taste.

Consequences for Remediation

An examination of some of the basic chemical characteristics (solubility, K_{oc} , Henry's Law Constant, etc.) will give an indication as to which remedial technologies can be used effectively for a specific

chemical. Before a remediation system can be designed for a site, you need to determine where the contaminants exist on a site, and in what concentrations. An air stripper designed to remove a specific concentration of MTBE may not function as designed if significant amounts of TAME are also present, and may not remove any of the TBA.

Action Levels/Cleanup Levels

The UST Branch plans to develop action levels or cleanup goals for TAME and TBA. Levels for TAME will be developed in the same general manner as was used for MTBE, primarily to prevent aesthetic impacts to drinking water (see Appendix 11, DERBCAP Guidance Document). The levels for TBA will be based on potential health risk. As for MTBE, the levels developed will be action levels, and are not necessarily cleanup goals. Cleanup goals will be assigned to sites on a site-by-site basis based on distances to actual or potential receptors and the types of receptors. \blacksquare

Editor's note: The March 2001 issue of LUSTLine has an article by Pat Ellis "A Circle Vicious-What do we know about the other oxygenates?" Contact the UST Branch for more information.

Survey Results

The last issue of *Think Tank* included a survey asking your opinion about the publication. Here are the results:

A full 79% say they read all the articles while 71% say they share *Think Tank* with others and 86% save it for future reference.

A whopping 93% of respondents rated the publication as either good or excellent.

Four percent thought articles were too detailed, 7% thought they were not detailed enough—the rest, 89%, found the content was just about right. And two-thirds of respondents wanted to see more graphics and illustrations in future issues.

Preference for future articles is as follows:

Cleanup	39%
Legal Issues	36%
Site Investigation	36%
Reporting Requirements	29%
Compliance	25%
ASTs	29%
Inspections	18%
Orphan tanks	14%
Leak Detection	7%
Vapor Recovery	7%

Dispenser Nozzle Automatic Shutoff Problems

by Peter Rollo

The number of complaints reported to the UST Branch about the failure of dispenser nozzles to shut off has been growing. Should a complaint be filed against your facility or if a customer complains in person that the nozzle failed to shut off, it is recommended that you follow the protocol outlined below. Simply replacing the old nozzle with a new one does not correct the problem in all occurrences.

Under Regulation 24, Section 36 of the Stage II Vapor Recovery Regulations, nozzles with no automatic overfill control mechanism or an inoperable overfill control mechanism are classified as "Defective Equipment". These nozzles shall be immediately and conspicuously posted as out of order until the problem is corrected.

Call the UST Branch and ask to speak to Peter Rollo, the Department's Environmental Engineer. Be prepared to describe which nozzle(s) failed and the circumstances leading to the nozzle failure. Based on that information you will be instructed on what to do to identify and correct the problem.

To return a nozzle to service you can generally proceed with the following steps:

1. Determine nozzle flow rate

The primary reason the nozzle fails to shut off is that the flow rate has dropped so low that the automatic shutoff device fails to close. Flow rates for all nozzles should be between 6–10 or 7–10 gpm depending on which CARB executive order your system is under. If the flow rate is in fact below 6 gpm, check the dispenser filters. The filters generally are to be replaced every six months at a minimum. High volume stations will need to do this more frequently. Check the product filters

and change out as necessary. If you are not sure what your change out frequency should be, check with the dispenser manufacturer. In most cases flow rates will return to normal at this point. If the flow rates are within the normal range proceed to step 2, otherwise proceed to step 3.

2. Verify function of the nozzle shutoff mechanism

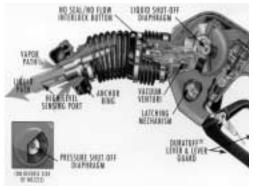
At the nozzle's lowest setting, dispense product into a bucket and immerse the spout into the liquid. It should immediately shut off. If the nozzle still does not shut off it should be replaced with a new nozzle or proceed to step 4.

3. Check function of related equipment

In some cases the piping, hoses or flow restrictors (if so equipped) become clogged. These should also be checked and cleaned as needed. If a problem is found here and the flow rates now return to normal levels, test the nozzle function as outlined in step 2.

4. Check Submersible Pump Function.

A subtle but more serious nozzle shutoff problem can occur during peak dispensing times. If nozzle shutoff problems are generally reported only during peak dispensing periods, it is an indication that the submersible product pump can no longer provide the correct flow during peak demand. Instead of an isolated nozzle, all nozzles at the facility may not function because the flow rate to all dispensers will be too low. During off peak periods, flow rates generally return to normal levels. This means nozzles that do not shut off during peak periods will function properly during off peak periods. The submersible product pumps need to be tested



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to determine whether or not they are functioning as they should.

5. Retain Defective Equipment

In addition to the nozzles, the Department requests that components found to be inoperable or defective not be thrown away when possible. Seal the defective component in a plastic bag and notify the Department's Environmental Engineer. You will be instructed how to proceed. In many cases the failed components can be a great help in diagnosing a problem. Manufacturers are also very interested in component failures and in many cases will analyze the failed component in their lab and provide a report as to why it failed. These results will be incorporated into future designs leading to higher quality products.

Please be aware that if any of the prescribed work outlined above is implemented, the facility's maintenance records should detail the problem and any corrective action. The corrective measures needed to return the nozzle to service are simple and the most cost effective. Simply replacing the old nozzle with a new one is generally a waste of money if the problem is not identified. Contact the Department for assistance and together this problem can be resolved quickly and economically.

THINK TANK

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Announcements

New Small Business Ombudsman: Kim Finch has been appointed the Small Business Ombudsman for DNREC. Kim works out of the Secretary's Office in the Business and Community Services section. The office of Ombudsman is separate from DNREC's regulatory program. As Ombudsman, Kim functions as a liaison between DNREC and the small business community. She is available to discuss compliance issues in a confidential manner and to provide assistance concerning environmental questions. Please contact Kim at (302) 739-6400 or by e-mail, kfinch@state.de.us, for assistance.

Of Note...

Consultants and students may be interested in an online remote sensing tutorial available from NASA: http://rst.gsfc.nasa.gov. It can be viewed and printed online and is also available on a CD-ROM. High-altitude images of the Earth are always fascinating. That's "distance learning!"

And a little closer to home is the digital National Atlas, available from the U.S. Geological Survey: http://nationalatlas.gov/natlas/natlasstart.asp. A viewer can click on a U.S. state or region of interest and "layer" the resulting map with a variety of data, ranging from "Agriculture" to "Water."

